Focus on selecting 300 series stainless steels for high temperature refinery services

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One aspect of refinery metallurgy is selecting the correct 300-series stainless steel for high temperature refinery environments. The primary corrosion concerns in high temperature refinery services are sulfidation corrosion and naphthenic acid corrosion.

Ironically, virtually any type of 300-series stainless steel will resist sulfidation corrosion—types 304, 304L, 316, 316L, 317, 317L, 321, and 347 all do a good job. This is not so for naphthenic acid corrosion (NAC) where only the molybdenum containing stainless steels (e.g., 316L, 317L) provide corrosion resistance more on NAC later.

So what is the problem? The problem is that during high temperature service, some of the above stainless steels will become "sensitized," which means they become susceptible to corrosion and cracking during shutdown conditions.

Figure 3

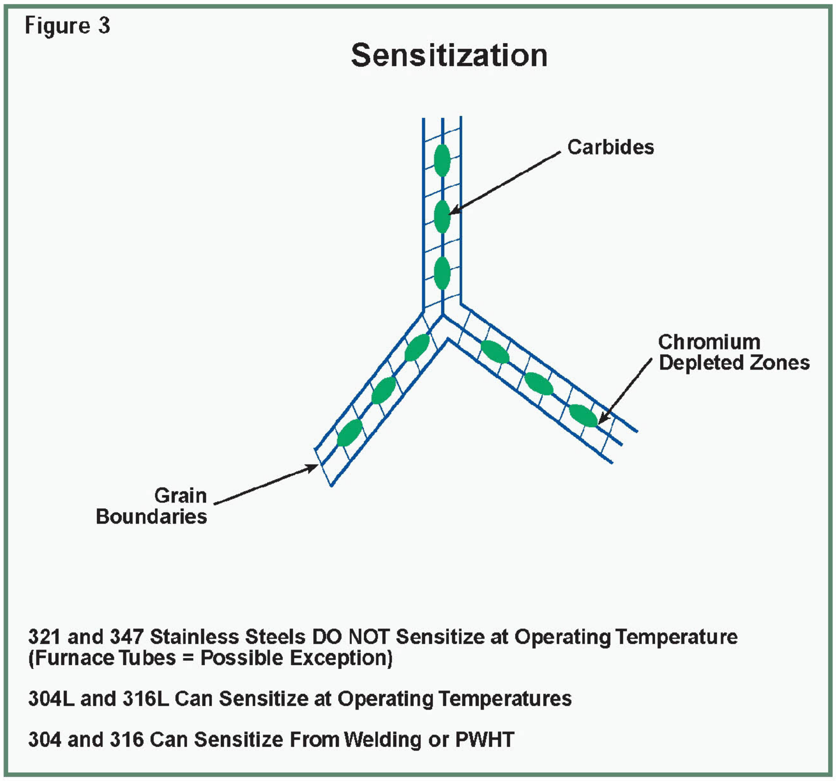

Figure 3: Sensitization of stainless steels

How does this sensitization occur? When certain stainless steels are exposed to temperatures greater than about 700F, the dissolved carbon combines with the chrome in the stainless steel to form chrome carbides. This happens most rapidly at the grain boundaries of the material (see Figure 3). So, immediately next to the grain boundaries, the stainless steel will be depleted in chrome and since *it's the chrome* that gives the stainless steel its corrosion resistance, we now have a zone that's "sensitive" to corrosion or cracking.

Sensitization is of no real concern at operating temperature since strength, mechanical properties and high temperature corrosion resistance are really not effected. However, sensitized stainless is sensitive to corrosion or cracking if it is exposed to moist conditions.

Moist conditions are almost always present during shutdowns unless special precautions are taken…and even then, it is difficult to keep conditions dry all the time. To make matters worse, the plants we are concerned with have sulfur contamination. The combination of sulfur scales (or sulfur coming out of insulation or refractory) and water forms sulfur acids, also called "polythionic acids." These acids can cause very rapid (like minutes or hours) cracking of sensitized stainless steel.

So what can we do to avoid "sensitizing" the stainless steel? One obvious step is to keep the carbon in the stainless steel low, so that it will not combine as much with the chrome. This is the idea behind the "low" carbon, or "L" grades of stainless, which limit the carbon content to less than 0.03%. Unfortunately, while this is good enough to avoid sensitization during the short time of welding, it is not good enough to avoid sensitization if the material is exposed to high temperatures (>700F) for many hundreds of hours.

This is where the "stabilized stainless steels" come in. Types 321 and 347 are "stabilized" stainless steels. Stabilized stainless steels add either titanium or columbium (also called niobium) to their chemistry

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Figure 4: Polythionic acid stress corrosion cracking of sensitized stainless steel

mix. Type 321 stainless uses titanium while Type 347 uses columbium. When heated, the carbon in the stainless will combine with the titanium or columbium more readily than it will with the chrome. Therefore the chrome is left alone, the material does not sensitize (it is "stable"), and everyone is happy.

Well, almost. It turns out that given enough time at a fairly narrow high temperature band, even Type 321 will sensitize…and even the super sensitization resistant Type 347 will sensitize at very long times (like years) in the right high temperature exposure band. Is this a practical problem for us?

In most cases, no. Type 321 SS will not sensitize below about 850F. Piping rarely sees temperatures above 800F, and we have found that 321 SS does well for hydroprocessing piping, for example. This is fortunate, because 347 is more expensive, and more difficult to fabricate, especially in thicknesses above about 3/4". But for items like furnace tubes, which do see metal temperatures above 850F, we must go to the best material for sensitization resistance (i.e., 347). Unfortunately, even 347 could sensitize at furnace operating conditions. Though rare, we have experienced polythionic stress corrosion cracking of 347 furnace tubes.

But don't give up—we have one more trick. If we ***"thermally stabilize"*** Type 347 stainless steel furnace tubes—by heating them to 1650F for 4 hours—then the mobility of the carbon is such that it just zips around like crazy, searching for any available columbium… soon there will be essentially no free carbon left at all. So you can then expose the stainless to high temperatures "forever" and it will not sensitize. Testing by Amoco showed that thermal stabilization worked "perfectly" for Type 347 SS and, to the extent you can trust any metallurgist, we "guarantee" that properly thermally stabilized 347 stainless will never sensitize at any time temperature combination.

Why do we hold for 4 hours at 1650F to thermally stabilize? Because we have always done it that way! We actually think that a 1650F +/- 25F temperature hold for something less than 4 hours would work, but we do not have the data to prove it. If a vendor claims they can do it effectively at less time, we need to insist on corrosion test data to backup the claim.

What if we weld in the field…do we need to restabilize the furnace tube after welding? Unfortunately, yes. The very high temperatures of welding puts all the carbides back into solution, so we need to "start over" and thermally stabilize the weld region. The set-up (heating coils, insulation, etc.) is just the same as for stress relieving.

Does thermally stabilizing the furnace tubes hurt the creep strength of the stainless? Good question—we do not think so. Literature data, vendor data, and some fairly long recent testing by Chevron on type 347 furnace tube material indicates that any reduction in creep strength is very small. To be conservative, we currently suggest for design purposes to reduce the "Larsen Miller Parameter" in the API 530 design curves by 1%. This means that the design metal temperature for a typical hydroprocessing furnace for a given tube thickness would be reduced by about 25F. (Heck, you shouldn't be running the furnace that close to the edge anyway!)

What about naphthenic acid corrosion (NAC)? Excluding NAC, we could summarize stainless steel selection for resisting high temperature sulfidation corrosion as follows:

Temperature	Steel Selection
Up to ~700F	Use 304L; 316L or 317L are also OK
700 to ~850F	Use 321
Above 850F, and particularly furnace tubes	Use thermally stabilized 347SS

But when NAC is an issue the above rules don't apply. We must use the molybdenum containing stainless steels, preferably 317L, to resist NAC attack regardless of operating temperature and accept the risk of polythionic acid cracking at shutdowns as the lesser of two evils. Shutdown precautions to prevent moisture contact become the primary defense against polythionic acid cracking in this case.

For more information on selecting stainless steels for high temperature refinery services, contact any company materials engineer. They all love this topic.